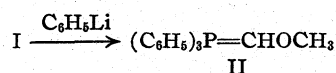
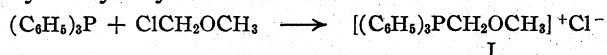


A NEW ALDEHYDE SYNTHESIS

Sir:

We have found that the Wittig olefin synthesis¹ can be extended to the synthesis of certain aldehydes by way of their enol ethers:



Triphenyl-(methoxymethyl)-phosphonium chloride (I) (m.p. 191–193°; Calcd for $\text{C}_{20}\text{H}_{20}\text{ClOP}$: Cl, 10.34. Found: Cl, 10.24) from triphenylphosphine and chloromethyl methyl ether, was finely powdered, suspended in anhydrous ether, and stirred under a nitrogen atmosphere while one equivalent of ethereal phenyl lithium was gradually added. The resulting deep red solution, presumably containing methoxymethylenetriphenylphosphorane (II) in two-fold excess, reacted with 5 α ,22 β ,25D-spirostan-3-one² (tigogenone), yielding 85% of 3-methoxymethylene-5 α ,22 β ,25D-spirostane (III) (m.p. 178–181°, $[\alpha]^{23}_{\text{D}} -65.8^\circ$, $\bar{\nu}_{\text{max}}$ 1683 cm^{-1} . Calcd. for $\text{C}_{29}\text{H}_{46}\text{O}_3$: C, 78.68; H, 10.47. Found: C, 78.90; H, 10.37). Brief treatment of this enol ether with diethyl ether, previously saturated with 72% perchloric acid, resulted in nearly quantitative hydrolysis to 5 α ,22 β ,25D-spirostane-3-carboxaldehyde (IV), as a mixture of epimers (m.p. 160–170°, $[\alpha]^{23}_{\text{D}} -57.4^\circ$, $\bar{\nu}_{\text{max}}$

(1) For leading references, see G. Wittig, *Angew. Chemie*, **68**, 505 (1956).

(2) R. W. Marker, T. Tsukamoto and D. L. Turner, *THIS JOURNAL*, **62**, 2525 (1940).

2693, 1731 cm^{-1} . Calcd. for $\text{C}_{28}\text{H}_{44}\text{O}_3$: C, 78.45; H, 10.34. Found: C, 78.59; H, 10.45).

This reaction sequence, when applied to the synthesis of the expected aldehydes from cyclohexanone and from acetophenone using a 100% excess of the reagent (II), resulted in incomplete reaction and lower over-all yields. Thus, from cyclohexanone, was obtained cyclohexanecarboxaldehyde 2,4-dinitrophenylhydrazone (40%), m.p. 172–173° alone or admixed with an authentic sample.³ Acetophenone was converted in similar over-all yield to hydratropaldehyde semicarbazone, m.p. 150–151° (lit.,⁴ 153–154°), which was further identified by direct conversion to the 2,4-dinitrophenylhydrazone, m.p. 134–135° (lit.,⁴ 135°).

The above synthetic method for the transformation $\text{—C=O} \rightarrow \text{—CHCHO}$ promises to offer certain advantages over the established glycidic ester sequence⁵: (1) milder reaction conditions; (2) avoidance of certain side reactions⁶; (3) possible utility of the enol ether intermediate as a “protected” aldehyde group or (4) as a starting substance for alternative transformations.

(3) Kindly furnished by Prof. W. S. Johnson.

(4) C. F. H. Allen and J. van Allan, *Organic Syntheses*, **24**, 87 (1944).

(5) Houben-Weil, “Methoden der Organischen Chemie,” Vol. VII, part 1, Georg Thieme Verlag, Stuttgart, 1954, p. 326.

(6) W. S. Johnson, J. S. Belew, L. J. Chinn and R. H. Hunt, *THIS JOURNAL*, **75**, 4995 (1953).

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